[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.]

Magnetic and Spectral Studies of the Structures of Some Methyl Isonitrile Complexes of Cobalt(II)

BY A. SACCO[1a] AND F. A. COTTON[1b]

RECEIVED JULY 21, 1961

Spectral and magnetic data are reported for methyl isonitrile complexes of cobalt(II). The compounds studied include two types previously reported by Sacco and Freni, *viz.*, (1) $Co(CH_3NC)_4X_2$ (X = Cl, Br, I), (2) $[Co(CH_3NC)_4][CoX_4]$ (X = Cl, Br, -NCS, as well as the new compounds $[Co(CH_3NC)_4][CdX_4]$ (X = Br and I). From the spectral and magnetic data, as well as X-ray powder studies which show that $[Co(CNCH_3)_4][CoBr_4]$ and $[Co(CNCH_3)_4][CdBr_4]$ are isomorphous, various more or less definite conclusions are reached about the structures of these complexes in the solid state, the chief ones being the following: (1) In all of the compounds studied there exist monomeric complex cations, $[Co(CH_3NC)_4]^{2+}$ and these exhibit effective magnetic moments of $\sim 1.85 \pm 0.05$ B.M. which are independent or nearly independent of temperature in the range 77 to 300°K. (2) On the basis of a correlation earlier suggested by Figgis and Nyholm, the relatively small orbital contribution to the moment of the $[Co(CH_3NC)_4]^{2+}$ complex cation implies that the ligand field is more nearly octahedral than tetragonal as a result of inclusion of halide ions or SCN^- ions—either free ones or those simultaneously incorporated in complex anions—in the coördination sphere of the cationic Co(II). The infrared spectra offer independent support for this structural proposal. (3) The detailed spectral and magnetic data provide conclusive support for Sacco and Freni's assignment of the $[Co(CH_3NC)][CoX_4]$ structure to the complexes of empirical formula $Co(CH_3NC)_2X_2$.

Introduction

Three stoichiometric classes of methyl isonitrile complexes of Co(II) have previously been reported by Sacco and Freni.[2] These are (1) the pentakis-(methylisonitrilo)-Co(II) series of which only the perchlorate salt, $Co(CH_3NC)_5(ClO_4)_2$, was prepared, (2) the tetrakis-(methylisonitrilo)-Co(II) series of general formula $Co(CH_3NC)_4X_2$, those with X = Cl, Br and I having been reported, and (3) the bis-(methyl isonitrilo)-Co(II) series, $Co(CH_3NC)_2X_2$, those with X = Cl, Br and SCN having been reported. $Co(CH_3NC)_5(ClO_4)_2$ was isolated in two forms, a stable, diamagnetic red form and a metastable (reverting to red), paramagnetic (1 unpaired electron) blue form. The $Co(CH_3NC)_4X_2$ compounds were all obtained as violet, paramagnetic (1 unpaired electron) compounds having electrical conductances and cryoscopic molecular weights in water consistent with their dissociation according to the equation

$$Co(CH_3NC)_4X_{2(s)} = [Co(CH_3NC)_4]^{2+}{}_{(aq)} + 2X^-{}_{(aq)}$$

The iodide, $Co(CH_3NC)_4I_2$, was also isolated in a diamagnetic olive-green form which changed over a period of several days into the stable paramagnetic violet form. Finally, it was shown by Sacco and Freni[2] that the "$Co(CH_3NC)_2X_2$" compounds are correctly formulated as $[Co(CH_3NC)_4][CoX_4]$. A little later Cotton and Holm[3] observed that while comparison of the magnetic moments reported by Sacco and Freni with the results of some then newly available data on the moments of the $[CoX_4]^{2-}$ species definitely supported the postulate that $[CoX_4]$ complex anions were present, they also raised the possibility that the cationically bound cobalt might be diamagnetic. This, if so, would be most easily explained by postulating dimeric complex cations, *viz.*, $[Co(CH_3NC)_4]_2{}^{4+}$. However, definite judgement on this was reserved until comparisons could be made among data all of which were obtained under the same conditions and standards of accuracy and treated by identical and entirely correct procedures in computing magnetic moments.

As this brief resume implies, several interesting structural problems are posed by these methyl isonitrile complexes of Co(II). This paper reports our efforts to solve those relating to the tetrakis-(methyl isonitrile)-cobalt(II) complexes using spectral and magnetic data. X-Ray structure determinations would of course offer more definite answers and would certainly be desirable, but none of these compounds can be obtained in the form of crystals suitable for such work. Thus, the indirect methods we have used will probably provide as much structural information as it appears possible to obtain at present.

Discussion

The $Co(CH_3NC)_4X_2$ Compounds.—Magnetic moments were measured over a range of temperature, and spectral data for all of these compounds were obtained, by the reflectance technique, by transmission through mulls in Nujol, or both.

The magnetic data for five compounds of this type, including the new ones in which X = $[CdBr_4]^{2-}$ and $[CdI_4]^{2-}$, are given in Table I. All of these moments are between 1.82 and 1.89 B. M., and according to the correlation suggested by Figgis and Nyholm[4] this indicates that the coördination is more nearly octahedral than planar. This would then mean that the three compounds in which X = Cl, Br and I should be written as $[Co(CH_3NC)_4X_2]$ indicating that the halide ions are coordinated to the Co(II). For the two tetrahalocadmiate salts one might postulate that halide ions form bridges, *i.e.*, are shared, between Co and Cd.

Attempts to prepare analogous Co(II) isonitrile compounds containing anions which would be less capable or incapable of bridging, *e.g.*, ClO_4^- and $[B(C_6H_5)_4]^-$, were, unfortunately, not successful. It has already been reported[2] that with perchlorate only the $[Co(CNR)_5]^{2+}$ salt can be isolated. In this work repeated attempts were made using $Co(NO_3)_2$, $Na[B(C_6H_5)_4]$ and CH_3NC with a variety of mole ratios, solvents and reaction conditions, but only $[Co(CH_3NC)_5][B(C_6H_5)_4]$ could

---

[1] (a) On leave from the Istituto di Chimica Generale dell' Universita di Milano; (b) Alfred P. Sloan Foundation Fellow.

[2] A. Sacco and M. Freni, *Gazz. Chim. Ital.*, **89**, 1800 (1959).

[3] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2983 (1960).

[4] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

TABLE I

MAGNETIC SUSCEPTIBILITIES[a] AND CALCULATED MAGNETIC MOMENTS FOR SEVERAL METHYL ISONITRILE COMPLEXES OF COBALT(II)

Compound	Temp. (°K.)	$\chi_{\mathrm{mol}}^{\mathrm{corr.}} \times 10^6$	Diamagnetic[b] corr. × 10^6	TIP[c] corr. × 10^6	μ, B.M.[d]	θ, °K.[d]
$[Co(CH_3NC)_4Cl_2]$	299	1,493 ± 26	137	..	1.89	0
	194	2,301 ± 28				
	77	5,804 ± 52				
$[Co(CH_3NC)_4Br_2]$	298	1,408 ± 28	157	..	1.84	0
	194	2,174 ± 31				
	77	5,460 ± 48				
$[Co(CH_3NC)_4I_2]$	296	1,504 ± 29	189	..	1.89	0
	195	2,272 ± 36				
	77	5,745 ± 65				
$[Co(CH_3NC)_4][CdBr_4]$	297	1,352 ± 20	251	..	1.82	− 8
	194	2,040 ± 16				
	77	4,780 ± 60				
$[Co(CH_3NC)_4][CdI_4]$	299	1,330 ± 15	315	..	1.82	−10
	195	2,008 ± 42				
	77	4,736 ± 64				
$[Co(CH_3NC)_4][CoCl_4]$	299	9,530 + 70	201	660	4.94[e]	−20
	194	14,200 ± 160				
	77	31,320 ± 280				
$[Co(CH_3NC)_4][CoBr_4]$	297	9,210 ± 35	241	735	4.87[e]	−20
	195	13,570 ± 60				
	77	30,480 ± 140				
$[Co(CH_3NC)_4][Co(NCS)_4]$	298	8,700 ± 80	225	460	4.73[e]	−20
	194	12,970 ± 120				
	77	28,330 ± 310				

[a] Susceptibilities were measured by the Gouy method as described in ref. 5. [b] Computed from Pascal's constants (*cf.* P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishing Co., New York, N. Y., 1956, p. 91). [c] Temperature-independent paramagnetism; computed for the CoX_4^{2-} ions from the relation TIP = 2.09/Δ as described in ref. 5. [d] These values were obtained by plotting $1/\chi_{\mathrm{mol}}^{\mathrm{corr}}$ *vs.* T(°K.). In all cases the points could be fitted within experimental error by a Curie–Weiss law $\mu = 2.84[\chi_{\mathrm{mol}}^{\mathrm{corr}}(T-\theta)]^{1/2}$. [e] These magnetic moments are only apparent ones obtained directly from the $\chi_{\mathrm{mol}}^{\mathrm{corr}}$ values with no attempt to partition the susceptibilities between cations and anions; they would also be the moments of the $CoX_4^{=}$ anions if the cations were diamagnetic. See Table II and the text for discussion of the partitioning.

be isolated. It would appear that the ability of the anions to function as bridges is an essential requirement in the compounds of the type $[Co(CNR)_4][MX_4]$.

In the work on the $[Co(CH_3NC)_4][CdX_4]$ compounds the possibility was considered that the cation might be diamagnetic due to dimerization with the susceptibility accidentally corresponding to a moment of ~ 1.85 B.M. due to the presence of ~ 15 atom % of cobalt substitutionally replacing Cd in the anion. Aside from the reproducibility of the magnetic susceptibility in several different preparations of the compound, very positive evidence that no significant amount of Co(II) was present in the anions was obtained from the reflectance spectrum of $[Co(CH_3NC)_4][CdBr_4]$. In this spectrum, Fig. 1, there is a distinct minimum in the spectral curve at ~ 700 mμ whereas the $[CoBr_4]^{2-}$ ion has a very strong ($\epsilon_{\max}$ ~ 700) absorption band centered at this wave length.

TABLE II

MAGNETIC MOMENTS OF $[CoX_4]^{2-}$ SPECIES AS OBSERVED IN OTHER COMPOUNDS AND AS COMPUTED UNDER TWO ASSUMPTIONS IN THE $[Co(CH_3NC)_4][CoX_4]$ COMPOUNDS

		Calculated μ in $[Co(CH_3NC)_4][CoX_4]$	
$[CoX_4]^{2-}$	Established range of μ, B.M.	Assuming cation diamagnetic	Assuming cation has μ = 1.82 B.M. at all temps.
$[CoCl_4]^{2-}$	4.50–4.70[5]	4.94	4.58
$[CoBr_4]^{2-}$	4.63–4.77[5]	4.87	4.55
$[Co(NCS)_4]^{2-}$	4.32–4.40[5]	4.73	4.35

The $[Co(CH_3NC)_4][CoX_4]$ Compounds.—The magnetic susceptibilities, electronic spectra and infrared spectra of three of these compounds, with X = Cl, Br and NCS, as well as data on the related $[Co(CH_3NC)_4][CdX_4]$ compounds enable us to reach some fairly definite conclusions regarding the structures of these compounds.

It may first be noted that reflectance and mull spectra of these compounds provide strong confirmation of Sacco and Freni's original suggestion that tetrahedral $[CoX_4]^{2-}$ ions are present. The ν_3 bands for each of these ions were observed to be in good agreement with the spectra of compounds known to contain $[CoX_4]^{2-}$ ions[5] as can be seen in Figs. 1, 2 and 3. Despite differences in the widths and contours of the bands among the three compounds, $[Co(CH_3NC)_4][Co(NCS)_4]$, $[N(CH_3)_4]_2[Co(NCS)_4]$ and $HgCo(NCS)_4$, it does appear that, qualitatively, the ligand field strength for the $[Co(NCS_4)^{2-}$ ion in the first compound is intermediate between those in the other two. This observation leads, on the basis of previous work on the latter two compounds,[5a] to the conclusion that, in the first compound, at least some of the SCN ions are bridging, which must mean that they are bound through their sulfur ends to the cobalt atoms in $Co(CH_3NC)_4^{2+}$ groups.

From the results discussed above for the $Co(CH_3NC)_4X_2$ and $Co(CH_3NC)_4CdX_4$ compounds,

---

(5) (a) F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961). (b) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *ibid.*, **83**, 4690 (1961).

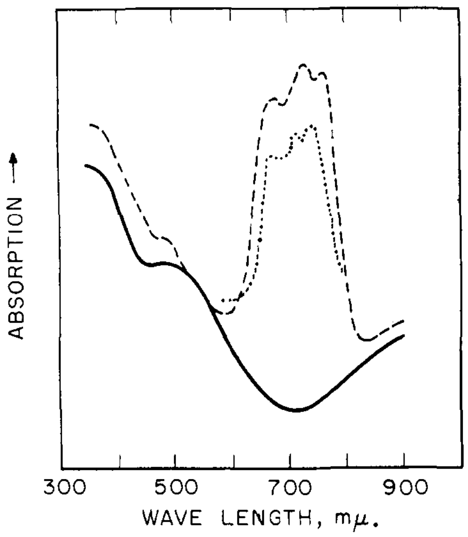

Fig. 1.—Reflectance spectra of $[Co(CNCH_3)_4][CdBr_4]$ (———), $[Co(CNCH_3)_4][CoBr_4]$ (-----------) and $(C_9H_8N)_2[CoBr_4]$, (..........).

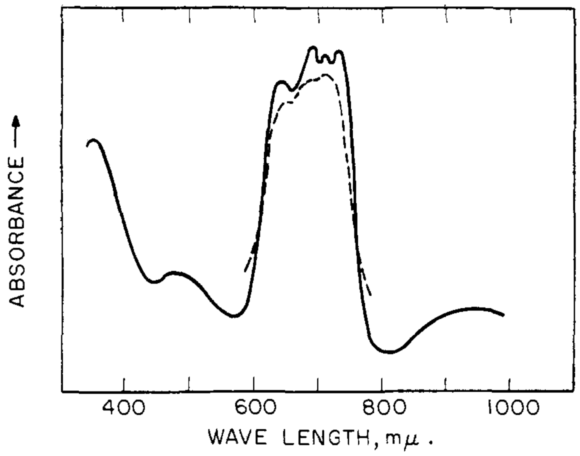

Fig. 2.—Reflectance spectra of $[Co(CNCH_3)_4][CoCl_4]$ (———) and $(C_9H_8N)[CoCl_4]$ (--------).

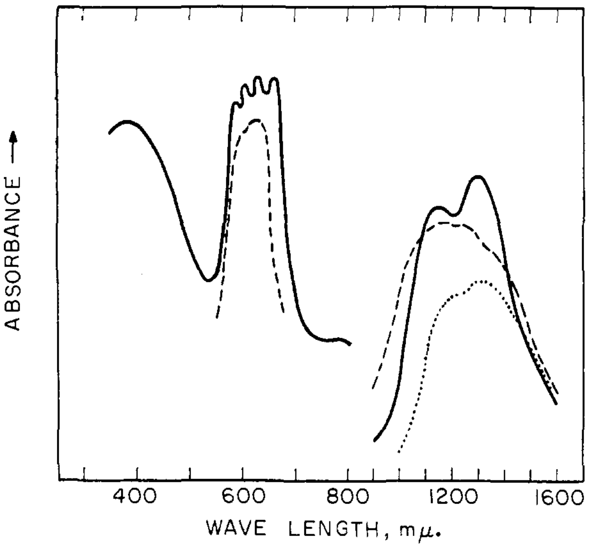

Fig. 3.—Reflectance spectra of $[Co(CNCH_3)_4][Co(NCS)_4]$ (———), $[N(CH_3)_4]_2[Co(NCS)_4]$ (--------) and $HgCo(NCS)_4$ (..........).

it is clear that in these compounds the $Co(CH_3NC)_4{}^{2+}$ ions are present as monomeric entities and that this complex cation has a magnetic moment of ~ 1.85 B. M. which is independent of temperature or nearly so. It is now possible to use the susceptibility data we have obtained for the $[Co(CH_3NC)_4][CoX_4]$ compounds (Table I) in comparison with the known magnetic properties of the $Co(CH_3NC)_4{}^{2+}$ cation and the $[CoX_4]^{2-}$ anions[5] to reach a conclusion about the structure of the cationic species in the $[Co(CH_3NC)_4][CoX_4]$ compounds. In Table II are recorded the established ranges for the moments of the $[CoX_4]^{2-}$ species[5] and the values calculated for them in the $[Co(CH_3NC)_4][CoX_4]$ compounds assuming first that the cationic complexes are diamagnetic as a result of dimerization and second that they make a contribution to the susceptibilities which is due to a temperature-invariant moment of 1.82 B. M. Contrary to the conclusion suggested[3] by the comparison of the earlier data of Sacco and Freni[2] for the $[Co(CH_3NC)_4][CoX_4]$ compounds with the earlier data of Holm and Cotton[3] the present study indicates quite definitely that the $[Co(CH_3NC)_4]^{2+}$ species exists as a monomeric paramagnetic entity with a magnetic moment of ~ 1.8 B.M. in the $[Co(CH_3NC)_4][CoX_4]$ compounds just as it does in the $Co(CH_3NC)_4X_2$ and $[Co(CH_3NC)_4][CdX_4]$ compounds.

In making the calculations assuming the $Co(CH_3NC)_4{}^{2+}$ groups to have temperature-invariant moments, we thus attribute the observed θ values entirely to the $[CoX_4]^{2-}$ species. While this may not be entirely correct, it is not unreasonable that the $[CoX_4]^{2-}$ ions might have such relatively large θ values in these compounds where we postulate that two X groups are bridges between Co atoms in $[CoX_4]^{2-}$ and $[Co(CH_3NC)_4]^{2+}$ while the other two are not. Figgis[6] has pointed out that distortions of the tetrahedral ligand fields in $[CoX_4]^{2-}$ ions are one likely cause of Weiss constants for these species. Bridging by half of the X groups in a $[CoX_4]^{2-}$ ion would probably introduce a small but significant distortion of the ion and hence of the tetrahedral ligand field at the Co(II) ion. It is also possible that the θ values reflect, at least in part, antiferromagnetic coupling between the cationic and anionic Co(II) ions which are connected by the bridges.

The infrared spectrum of $[Co(CH_3NC)_4][Co(NCS)_4]$ affords some definite evidence for the halide (or pseudohalide) bridging postulated earlier for the $[Co(CH_3NC)_4][CdX_4]$ compounds and also postulated here for the $[Co(CH_3NC)_4][CoX_4]$ compounds. Two strong bands are found in the region characteristic of the CN stretching modes for coordinated thiocyanate ion, namely, at 2102 and 2072 cm.$^{-1}$. Measurements of the band positions in several other $[Co(NCS)_4]^{2-}$ compounds[7] as well as results reported for other types of thiocyanate complexes[8] have shown a definite correla-

---

[6] B. N. Figgis, *Trans. Faraday Soc.*, **65**, 1553 (1960).

[7] D. M. L. Goodgame, unpublished observations using a spectrometer equipped with fluorite optics.

[8] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

tion between the frequency of the CN stretching band and the attachment of the sulfur end of the SCN group to another metal ion. Thus in $K_2[Co(NCS)_4]$ the band is at 2066 cm.$^{-1}$ and in $(Me_4N)_2[Co(NCS)_4]$ at 2075 cm.$^{-1}$ whereas in $HgCo(NCS)_4$, where all sulfur atoms are attached to the strongly sulfur-binding Hg^{2+} ion, the frequency is 2141 cm.$^{-1}$. We interpret the spectrum of $[Co(CH_3NC)_4][Co(NCS)_4]$ by assigning the band at 2072 cm.$^{-1}$ to $-NCS$ groups which have free sulfur ends and the band at 2102 cm.$^{-1}$ to —NCS groups with sulfur ends coordinated to Co atoms in the $[Co(CH_3NC)_4]^{2+}$ cations.

X-Ray Evidence.—It has also been found from comparison of the X-ray powder diffraction patterns of $[Co(CNCH_3)_4][CoBr_4]$ and $[Co(CNCH_3)_4][CdBr_4]$ that these two compounds are isostructural. This provides independent evidence in support of the conclusions drawn above as to the presence of $[CoX_4]^{2-}$ anions in the compounds of stoichiommetry $Co(CNCH_3)_2X_2$.

Infrared Spectra.—The positions of the isonitrile NC stretching bands in the infrared spectra of all of the compounds studied here may be correlated with the assumed molecular and electronic structures of the compounds. The basis for these correlations was established previously by Cotton and Zingales.[9] The CN frequencies for the methyl isonitrile complexes of cobalt(II) are summarized in Table III. It has already been shown that the order of the frequencies of the CN stretching modes in two isonitrile complexes which differ only in the *formal* charge on the metal atom will be the same as the order of formal charges. This is because the tendency of the metal to donate electrons from its dπ orbitals to the CN antibonding orbitals is inversely proportional to the positive charge on the metal atom and the CN bond order is inversely proportional to the degree of occupancy of its antibonding orbitals. The principles involved lead one to expect that in two complexes, $M(RNC)_nX_m$ and $M(RNC)_nY_m$, with the metal atom in the same formal oxidation state in both, the CN frequencies would vary directly with the *effective* charge on M; this in turn would vary inversely with the degree to which the groups X and Y donate charge to M.

Table III

Isonitrile NC Stretching Frequencies[a] in Complexes Containing $[Co(CH_3NC)_4]^{2+}$

Compound (L = CH_3NC)	ν_{NC}, cm.$^{-1}$
CoL_4Cl_2	2227
CoL_4Br_2	2230
CoL_4I_2 (violet)	2233
$CoL_4[CoCl_4]$	2260
$CoL_4[CoBr_4]$	2255
$CoL_4[Co(NCS)_4]$	2248
$ClL_4[CdBr_4]$	2258
$CoL_4[CdI_4]$	2252
CH_3NC	2165–2170[b]

[a] All spectra were obtained using a Baird Infrared Spectrophotometer equipped with a fluorite prism. The spectra were calibrated with polystyrene and the frequencies are believed to be accurate to ± 3 cm.$^{-1}$. [b] In hydrocarbons or other non-polar solvent and in the gas phase. Polar solvents, *e.g.*, $CHCl_3$, affect the frequency noticeably.

A definite correlation of this kind is found for the six compounds containing the $Co(CH_3NC)_4{}^{2+}$ grouping. Thus in the $[Co(CH_3NC)_4X_2]$ (X = Cl, Br, I) compounds the CN frequencies are all 2230 ± 3 cm^{-1}. In $[Co(CH_3NC)_4][CoCl_4]$, $[Co(CH_3NC)_4][CoBr_4]$, $[Co(CH_3NC)_4][CdBr_4]$ and $[Co(CH_3NC)_4][CdI_4]$ the CN frequencies are practically equal within experimental error (2256 ± 4 cm.$^{-1}$), but the average is significantly higher (26 cm.$^{-1}$) than for the $[Co(CH_3NC)_4X_2]$ compounds. This difference is in the direction expected considering that the halide ions which are already bound in the complex anions, $[CoX_4]^{2-}$ and $[CdX_4]^{2-}$, should certainly be poorer donors to the cobalt in $Co(CH_3NC)_4{}^{2+}$. That the isonitrile CN frequency should be lowest among all of the $[Co(CH_3NC)_4][MX_4]$ compounds when X is thiocyanate is reasonable since this ligand uses different atoms to form the two bonds to metal atoms and is thus best able to form two bonds simultaneously.

Experimental

Preparation of Compounds. **$(CH_3NC)_4CoCdBr_4$.**—A solution of anhydrous cobalt bromide (1.6 g., 0.007 mole) in methyl alcohol (100 ml.) was added, drop by drop and with stirring, to a solution of cadmium bromide tetrahydrate (6.9 g., 0.020 mole) and methylisonitrile (1.3 g., 0.031 mole) also in methyl alcohol (120 ml.). After addition of a few drops of the methyl alcoholic solution of $CoBr_2$, a pink, crystalline compound began to precipitate, together with some blue crystals. After filtration, the compound was suspended in methyl alcohol and the suspension boiled until complete disappearance of any blue crystals. After filtration, the product was washed with methanol and dried in vacuum; yield, 4.0 g., m.p. 245° dec.

Anal. Calcd. for $C_8H_{12}N_4Br_4CoCd$: C, 14.66; H, 1.85; N, 8.55; Co, 9.00. Found: C, 14.42; H, 1.83; N, 8.50; Co, 9.27.

The compound was soluble in water, giving a blue solution; insoluble in all the organic solvents tested.

$(CH_3NC)_4CoCdI_4$.—This was prepared in essentially the same manner as the analogous bromide. To 0.75 g. (0.08 mole) of methylisonitrile and 3.7 g. (0.010 mole) of cadmium iodide dissolved in 80 ml. of methanol, a solution of 1.25 g. (0.004 mole) of anhydrous cobalt iodide in 80 ml. of methanol was added slowly with stirring. The light brown precipitate obtained was filtered, washed with methanol and dried in vacuum; yield, 3.0 g., m.p. >260°.

Anal. Calcd. for $C_8H_{12}N_4I_4CoCd$: C, 11.39; H, 1.43; N, 6.65. Found: C, 11.12; H, 1.38; N, 6.53.

$[Co(CH_3NC)_4][Co(NCS)_4]$.—To a solution of 4.0 g. (0.023 mole) of $Co(NCS)_2$ in 60 ml. of methanol, a solution of methylisonitrile (1.6 g., 0.039 mole) in 80 ml. of methanol was slowly added with stirring. The fine green precipitate obtained was filtered, washed with methanol and dried in vacuum; yield, 4.2 g.

Anal. Calcd. for $C_6H_6N_4S_2Co$: C, 28.02; H, 2.35; N, 21.78. Found: C, 27.84; H, 2.27; N, 21.60.

$[Co(CH_3NC)_5][B(C_6H_5)_4]_2$.—To a solution of 1.20 g. (0.004 mole) of $Co(NO_3)_2 \cdot 6H_2O$ and 3.80 (0.012 mole) of $Na[B(C_6H_5)_4]$ in 60 ml. of acetone, a solution of methylisonitrile (0.33 g., 0.008 mole) in 60 ml. of acetone was slowly added with stirring. The red-brown precipitate obtained was filtered, washed with methanol and dried in vacuum; yield, 1.2 g., m.p. 135–137°.

Anal. Calcd. for $C_{58}H_{55}N_5B_2Co$: C, 77.18; H, 6.14; N, 7.76. Found: C, 76.89; H, 6.20; N, 7.80. The compound is soluble in hot acetone giving a brown solution, slightly soluble in cold acetone, insoluble in all other organic solvents tested.

All the other compounds were prepared as previously described.[2]

---

(9) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

Acknowledgments.—We thank The Research Corporation and the Alfred P. Sloan Foundation for generous financial aid and Drs. D. M. L. Goodgame and M. Goodgame for useful discussion and cooperation in some of the spectral measurements.

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

A Calorimetric Study of the Reaction of Rare-earth Ions with EDTA in Aqueous Solution[1]

BY J. L. MACKEY, J. E. POWELL AND F. H. SPEDDING

RECEIVED SEPTEMBER 23, 1961

The heats of reaction for the rare earths with EDTA in solution at 25° and $\mu = 0.1\ M$ (KNO_3) have been measured using a calorimetric method. The method was based on the replacement of one chelated metal ion by another and offers several advantages for studies of EDTA-like ligands. The thermodynamic quantities ΔF^0, ΔH^0 and ΔS^0 for the reaction of rare-earth ions with EDTA in 0.1 M KNO_3 are reported. These quantities indicate that the rare-earth chelates of EDTA fall into two series. Reasons for the existence of the two series were discussed, and it was suggested that a basic trend in ΔH^0 occurs in the rare-earth series, which is independent of the complexing or chelating ligand.

Introduction

Studies of metal complexes and chelates in solution have been confined primarily to the determination of the stability constants of species formed from metal ions and various ligands and correlation of these constants with ionic properties such as radius, charge, electronegativity and electronic structure. Recently, however, experimental studies have been concerned with a more complete thermodynamic description of complex and chelate formation. In addition to the free energies of formation of the complex species, which are derived from formation constants, measurements of the heats of reaction have been made. Knowing these quantities, entropy changes can be calculated from the equation

$$\Delta F = \Delta H - T\Delta S$$

ΔH's are generally determined either from the temperature dependence of the equilibrium constant or by direct calorimetric measurements.

In view of many recent studies of the stability constants of complexes and chelates of the rare-earth elements and the current interest in correlating and explaining the orders of stability observed, it seemed appropriate to measure the thermodynamic quantities of chelate formation for a complete rare-earth series. In this paper we report data for ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA), which was the first chelating agent for which all the rare-earth–chelate stability constants were obtained.[2]

Studies of the heats and entropies of reaction of a number of bivalent metal ions with EDTA have appeared,[3] and Staveley and Randall[4] have reported values for six trivalent metals including cerium, neodymium, gadolinium and yttrium. Betts and Dahlinger[5] have reported the heats and entropies of association of the rare earths with EDTA using a method based on the temperature dependence of the equilibrium constants for exchange reactions of the type

$$ACh^- + B^{3+} \rightleftarrows BCh^- + A^{3+}$$

The exchange constants at various temperatures were determined by radiochemical techniques. The accuracy of the data is subject to the usual limitations of the temperature-dependence method, such as the limited temperature range available and the small variation in log K with temperature. The method used also introduced a cumulative uncertainty into the values of ΔH since the exchange reactions had to be measured progressively. The value for lutetium, for example, was obtained from the Lu–Yb exchange and the value for ytterbium was obtained from the Yb–Er exchange, etc. This led to a possible error in the case of lutetium nearly as large as ΔH itself. A considerable difference was observed between the temperature-dependence values and those determined calorimetrically by Staveley and Randall. Consequently, it was desirable to redetermine the heats for the formation of the rare-earth chelates in solution using a calorimetric method.

Experimental

The calorimetric method used in this work differed somewhat from the method used by Staveley, *et al.*[3b,4] Their procedure required first the measurement of the enthalpy change for the addition of a slight excess of EDTA (primarily the tetrapotassium salt) to a solution of the metallic nitrate in 0.1 M KNO_3. Enough dilute nitric acid was added to give a final pH of 4.5. Next, the same amount of EDTA was added to a solution without the metallic nitrate, but otherwise the same. In order to calculate the heat of chelation of the metal ion with EDTA in solution, it was necessary to determine the pH's of the initial and final solutions accurately, because it was necessary to consider the third and fourth ionization constants of EDTA and the enthalpy changes associated with these ionizations. Due to the uncertainties related to pH dependence, it seemed advantageous to employ a calorimetric method which allows a more direct comparison of the heats of reaction of the rare earths with EDTA.

The method used in the present work was based on the replacement of one chelated metal ion by another. The procedure consisted of three steps. First, the change in heat content was measured when a relatively concentrated solution of magnesium chelate at its neutral equivalence

---

[1] Contribution No. 1065. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).

[3] (a) R. C. Charles, *ibid.*, **76**, 5854 (1954); (b) L. A. K. Staveley and R. A. Care, *J. Chem. Soc.*, 4571 (1956).

[4] L. A. K. Staveley and T. Randall, *Discussions Faraday Soc.*, No. 26, 157 (1958).

[5] R. H. Betts and O. F. Dahlinger, *Can. J. Chem.*, **37**, 91 (1959).